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(54) Process for the preparation of amorphous polymers of propylene

Verfahren zur Herstellung von amorphen Propylenpolymeren

Procédé pour la préparation de polymères amorphes de propylène

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[0001] The present invention relates to a process for the preparation of amorphous polymers of propylene.

[0002] The invention also relates to a process for the preparation of indene compounds suitable as metallocene ligands.

[0003] As it is well known, products of the propylene homopolymerization can be either crystalline or amorphous. Whereas the polypropylene having isotactic or syndiotactic structure is crystalline, the polypropylene having essentially atactic structure appears to be amorphous. The atactic polypropylene, in the representation by the Fischer formula as described in "M. Farina, Topics Stereochem., 17, (1987), 1-111" shows methyl groups casually arranged from one or the other side of the polymeric chain. As described in the above mentioned publication, useful information on the structure can be obtained from the N.M.R. analysis.

[0004] The amorphous polypropylene available on the market is mainly used in adhesive compositions and as additives for bitumens. Generally, it is a by-product of the isotactic polypropylene obtained in the presence of catalysts of the Ziegler-Natta type. The separation of small fractions of amorphous polypropylene from the remainder product however involves inconvenient separation processes with solvents.

[0005] More recently, in the polymerization reaction of the olefins, catalysts based on metallocene compounds and alumoxane compounds have been used. Operating in the presence of these catalysts, polymers characterized by a narrow molecular weight distribution and endowed with structural characteristics of interest can be obtained.

[0006] In particular, by polymerizing propylene in the presence of metallocene catalysts, depending on the metallocene used crystalline or amorphous polypropylene can be obtained. However, the amorphous polypropylene obtainable in the presence of metallocene catalysts is generally endowed with low molecular weight.

[0007] U.S. Patent 4,542,199 describes a catalytic system for the polymerization of olefins comprising a bis(cyclopentadienyl)zirconium and an alumoxane. From the polymerization reaction of propylene carried out in the presence of this catalyst, low molecular weight atactic polypropylene is obtained.

[0008] European patent application 283,739 describes a catalytic system for the polymerization of olefins comprising a partially substituted bis(cyclopentadienyl)zirconium and an alumoxane. From the polymerization reaction of propylene carried out in the presence of this catalyst, low molecular weight atactic polypropylene is obtained.

[0009] In U.S. Patent 4,931,417, catalysts for the polymerization of olefins comprising a metallocene compound wherein two cyclopentadienyl rings are joined through a radical containing a silicon or germanium atom are described. The polymerization reaction of propylene carried out in the presence of these compounds partially substituted on the cyclopentadienyl rings gives rise to isotactic polypropylene, whereas with dimethylsilandiylbis(cyclopentadienyl)zirconium dichloride, low molecular weight atactic polypropylene is obtained.

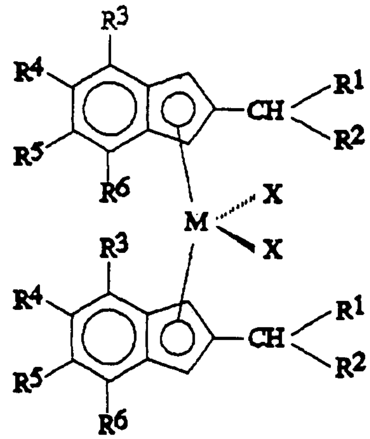
[0010] In European patent application 399,347 a process for the polymerization of propylene in the presence of a catalyst comprising a metallocene having a cyclopentadienyl ring and a fluorenyl ring joined by a bridge, such as isopropylidene-(9-fluorenyl)(3-methylcyclopentadienyl)zirconium dichloride is described. An amorphous polypropylene is obtained, the structure of which however is not atactic, but is defined as syndioisoblocks. Namely, it is a structure wherein syndiotactic and atactic sequences alternate.

[0011] The international application WO 94/11406 describes a class of indenyl compounds substituted in the 2-position on the indenyl group. In the application it is stated that this compounds can be used as catalyst components for the polymerization of olefins. However, in the polymerization examples only homopolymers of ethylene and elastomeric copolymers of ethylene with propylene are prepared.

[0012] It has now been found that it is possible to prepare substantially amorphous polymers of propylene having high molecular weight, operating at temperatures of industrial interest, by carrying out the polymerization reaction of propylene in the presence of metallocene catalysts comprising particular bis-indenyl or bis-4,5,6,7-tetrahydroindenyl compounds substituted in the 2-position on the indenyl or tetrahydroindenyl groups.

[0013] Therefore, an object of the present invention consists of a process for the preparation of substantially amorphous polymers of propylene having melting euthalpies (ΔH_f) that are not measurable by differential scanning calorimetry comprising the polymerization reaction of propylene and optionally one or more olefins to obtain a homopolymer of propylene or a copolymer of propylene having up to 10% by mole of comonomeric units, said polymerization being carried out in the presence of a catalyst comprising the product of the reaction between:

(A) a metallocene compound selected from the bis-indenyl compounds of formula (I):



(I)

and the corresponding bis-4,5,6,7-tetrahydroindenyl compounds, wherein:

on each indenyl or tetrahydroindenyl group the substituents R^1 and R^2, same or different from each other, are hydrogen atoms, $-CHR_2$ groups or -CHR- groups joined between them to form a cycle comprising from 3 to 8 carbon atoms, wherein the R substituents are hydrogen atoms, C_1-C_{20} alkyl radicals, C_3-C_{20} cycloalkyl radicals, C_2-C_{20} alkenyl radicals, C_6-C_{20} aryl radicals, C_7-C_{20} alkaryl radicals or C_7-C_{20} aralkyl radicals and can contain Si or Ge atoms;
the substituents R^3, R^4, R^5 and R^6, same or different from each other, are defined as R substituents, in addition two adjacent R^3, R^4, R^5 and R^6 substituents on the same ring can form a ring comprising from 5 to 8 carbon atoms;
M is a transition metal atom of groups IVb, Vb or VIb of the Periodic Table;
substituents X, same or different from each other, are hydrogen atoms, halogen atoms, $-R^7$, $-OR^7$, $-SR^7$, $-NR^7_2$ or-PR^7_2 groups where substituent R^7 are defined as substituent R; optionally pre-reacted with an organometallic compound of aluminium of formula AlR^8_3 or $Al_2R^8_6$, wherein substituents R^8, same or different, are defined as substituent R or are halogen atoms; and

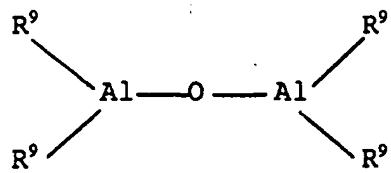
(B) at least a compound selected among the organo-metallic compounds of aluminium containing at least an heteroatom selected from oxygen nitrogen and sulphur, optionally in admixture with an organometallic compound of aluminium of formula AlR^8_3 or $Al_2R^8_6$, wherein substituents R^8, same or different, are defined as above, and between the compounds able to give a metallocene alkyl cation.

[0014] Among the metallocene compounds of formula (I), the preferred are those wherein, in each of the indenyl or tetrahydroindenyl groups the substituents R^3 are the same as substituents R^6, and substituents R^4 are the same as substituents R^5. More preferred are those in which all the substituents R^3 and R^6 are hydrogen atoms.
[0015] The transition metals, M is preferably selected between titanium, zirconium, hafnium and vanadium, more preferably being zirconium.
[0016] The substituents X are preferably chlorine atoms or a methyl radical.
[0017] Non limiting examples of metallocene compounds which can be used in the process of the present invention are:

bis(2-methyl-indenyl)zirconium dichloride,
bis(2,4,7-trimethyl-indenyl)zirconium dichloride,
bis(2,4,6-trimethyl-indenyl)zirconium dichloride,
bis(2,5,6-trimethyl-indenyl)zirconium dichloride,
bis(2,4,5,6,7-pentamethyl-indenyl)zirconium dichloride,
bis(2-ethyl-indenyl)zirconium dichloride,
bis(2-ethyl-4,7-dimethyl-indenyl)zirconium dichloride,
bis(2-ethyl-4,6-dimethyl-indenyl)zirconium dichloride,
bis(2-ethyl-5,6-dimethyl-indenyl)zirconium dichloride,
bis(2-ethyl-4,5,6,7-tetramethyl-indenyl)zirconium dichloride,

bis(2-propyl-indenyl)zirconium dichloride,
bis(2-propyl-4,7-dimethyl-indenyl)zirconium dichloride,
bis(2-propyl-4,6-dimethyl-indenyl)zirconium dichloride,
bis(2-propyl-5,6-dimethyl-indenyl)zirconium dichloride,
bis(2-propyl-4,5,6,7-tetramethyl-indenyl)zirconium dichloride, bis(2-methyl-indenyl)zirconium dimethyl,
bis(2,4,7-trimethyl-indenyl)zirconium dimethyl,
bis(2,4,6-trimethyl-indenyl)zirconium dimethyl,
bis(2,5,6-trimethyl-indenyl)zirconium dimethyl,
bis(2,4,5,6,7-pentamethyl-indenyl)zirconium dimethyl,
and the corresponding bis-4,5,6,7-tetrahydroindenyl compounds.

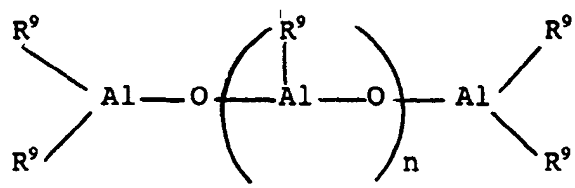
[0018] Alumoxanes usable in the catalyst of the invention are, for example, linear, cyclic or branched alumoxanes containing at least one group of the type (II):



(II)

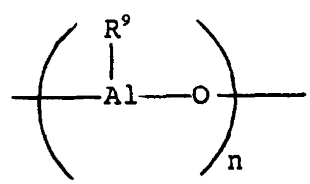
where the substituent R^9, same or different from each other, are R^1 or a group $-O-Al(R^9)_2$, and optionally some R^9 may be halogen atoms.

[0019] In particular, alumoxanes of formula (III) may be used:



(III)

in the case of linear compounds where n is 0 or an integer comprised between 1 and 40 and the substituents R^9 are defined as substituents R^1, or alumoxanes of formula (IV):



(IV)

in the case of cyclic compounds, with n which is an integer comprised between 2 and 40, and the substituents R^9 are defined as the substituents R^1.

[0020] Substituents R^9 are preferably methyl, ethyl, isobutyl.

[0021] Examples of alumoxanes suitable to be used according to the present invention are methylalumoxane (MAO) and isobutylalumoxane (TIBAO).

[0022] The alumoxanes used in the process of the present invention may be obtained by reaction between water and a organometallic compound of aluminium of formula AlR^8_3 or $Al_2R^8_6$, in which the substituents R^8, same or different from each other, are defined as above, with the condition that at least one R^8 is different from halogen. In that case these are made to react in a molar ratio of Al/water comprised between about 1:1 and 100:1.

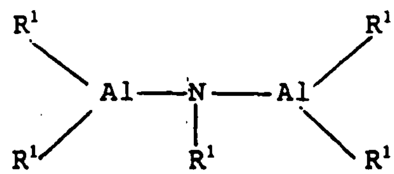
[0023] Non limiting examples of the aluminium compound of formula AlR^8_3 or $Al_2R^8_6$ are:

$Al(Me)_3$, $Al(Et)_3$, $AlH(Et)_2$, $Al(iBu)_3$, $AlH(iBu)_2$, $Al(iHe)_3$,
$Al(C_6H_5)_3$, $Al(CH_2C_6H_5)_3$, $Al(CH_2CMe_3)_3$, $Al(CH_2SiMe_3)_3$, $Al(Me)_2iBu$,

$Al(Me)_2Et$, $AlMe(Et)_2$, $AlMe(iBu)_2$, $Al(Me)_2iBu$, $Al(Me)_2Cl$, $Al(Et)_2Cl$, $AlEtCl_2$, $Al_2(Et)_3Cl_3$, where Me=methyl, Et=ethyl, iBu-=isobutyl, iHe=hexyl. Trimethyl aluminium (TMA) and triisobutyl aluminium (TIBAL) are preferred.

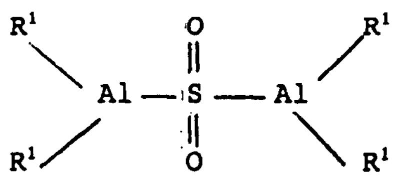
[0024] A particular class of organo-metallic compounds of aluminium used in the catalyst according to the invention is those obtainable by the reaction of water with the aluminium alkyl or alkylhydride in which at least one alkyl is not linear, in a molar ratio Al/H_2O comprised between 1:1 and 100:1. Compounds of this type are described in the European patent application No. EP-575.875, the content of which is herein intended as incorporated in the present description.

[0025] Organo-metallic compounds of aluminium useable in the catalyst according to the invention are, in addition, those of formula (V):



(V)

or of formula (VI):



(VI)

where R^1 is defined as above.

[0026] The molar ratio between the aluminium and the metal of the metallocene compound is in general comprised between about 10:1 and about 10000:1, and preferably between about 100:1 and about 5000:1.

[0027] Non limiting examples of the compound capable of forming alkyl metallocene cations are compounds of formula Y^+Z^-, where Y^+ is a Brönsted acid, capable of donating a proton and of irreversibly reacting with substituent X^1 or X^2 of the compound of formula (I) and Z^- is a compatible anion, which does not coordinate, which is capable of stabilising the active catalytic species which originates from the reaction of the two compounds, and is sufficiently labile in order to be removed by an olefinic substrate. Preferably the anion Z^- comprises one or more boron atoms. More preferably the anion Z^- is an anion of formula $BAr_4^{(1)}$, where the substituents Ar, same or different from each other, are aryl radicals such as phenyl, pentafluorophenyl, bis(trifluoromethyl)phenyl. Particularly preferred is the tetrakis-pentafluorophenyl-borate. In addition, compounds of formula BAr_3 may be conveniently used. compounds of this type are described, for example, in the published International patent application WO 92/00333, the content of which is incorporated in the present description.

[0028] The catalysts of the present invention may also be used on inert supports. That is what is obtained by depositing the metallocene compound (A), or the product of reaction of the latter with component (B), or component (B) and subsequently the metallocene compound (A), on an inert support such as, for example silica, alumina, styrene-divinylbenzene copolymer, polyethylene or polypropylene.

[0029] A particularly suitable class of inert supports used in the process of the present invention are porous organic supports functionalized with functional groups having active hydrogen atoms. Particularly preferred are those in which the organic support is a partially crosslinked styrene polymer. These supports are described in the European patent application EP-633,272.

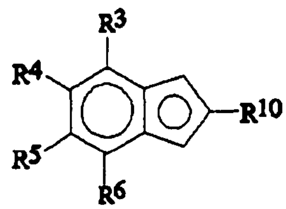
[0030] The solid so obtained, in combination with further additions of the alkyl aluminium compound is either as such or pre-reacted with water, if necessary, is usefully used in gas phase polymerisation.

[0031] The metallocene compounds of formula (I) can be prepared by reaction of the corresponding indenyl or tetrahydroindenyl ligands with a compound able to form a delocalized anion on the cyclopentadienyl ring, and then with a compound of formula MX_4, wherein M and the substituents X are defined as above.

[0032] In the case in which at least a substituent X of the metallocene compound of formula (I) to be prepared is different from an halogen, it is necessary to substitute at least a substituent X in the obtained metallocene with at least a substituent X different from halogen.

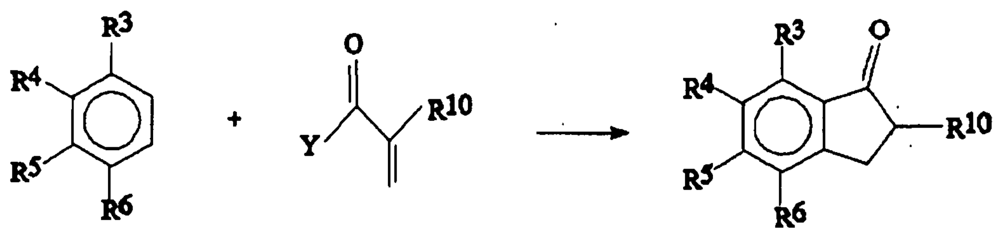
[0033] The reaction of substitution of substituents X with substituents X different from halog n is carried out with commonly known methods. For instance, when the desired substituents X are alkyl groups, the metallocenes can be allowed to react with alkylmagnesium halides (Grignard reactives) or with lithioalkyl compounds.

[0034] A particularly advantageous process for the preparation of indene compounds of formula (VII):



(VII)

suitable as metallocene ligands, comprises the reaction of an aromatic compound of formula (VIII) with a compound of formula (IX), to obtain the indan-1-one of formula (X), wherein R^3, R^4, R^5 and R^6 have the above defined meaning, R^{10} is an hydrogen atom or an alkyl radical C_1-C_3, Y is an halogen atom, according to the following reaction scheme:



(VIII) (IX) (X)

and the following conversion into the corresponding indene (VII).

[0035] The indan-1-ones (X) can be converted in the corresponding indenes (VII) by different methods.

[0036] For instance, the indan-1-ones (X) can first be converted to the indan-1-oles and than dehydrated.

[0037] Reducing agents suitable to be used in the reduction reaction are, for instance, lithium aluminium hydride and sodium boron hydride.

[0038] The dehydration reaction can be performed in the presence of an acid such as, for instance, p-toluene-sulphonic acid.

[0039] The propylene polymers obtainable with the process of the present invention are endowed with an atactic structure and, therefore, they are substantially amorphous. Their melting enthalpy (ΔH_f) is generally not measurable.

[0040] The molecular weight of the above said propylene polymers can even be very high. In fact the intrinsic viscosity can reach very high values, up to 10 dl/g and above.

[0041] The molecular weights of the propylene polymers, in addition to being high, are distributed over relatively limited ranges. An index of molecular weight distribution is represented by the ratio M_w/M_n which is preferably less than 4, more preferably less than 3.

[0042] ^{13}C-N.M.R. analysis gives information on the tacticity of the polymeric chain, that is the distribution of the relative configuration of the tertiary carbons.

[0043] The structure of the propylene polymer appears substantially atactic. Nevertheless, it is observed that the isotactic diads (m) appear to be more numerous than the syndiotactic diads (r). Namely, %(m) - %(r) > 0, preferably %(m)- %(r) > 5 and, more preferably %(m) - %(r) > 10.

[0044] The Bernoullianity index (B), defined as:

$$B = 4\,[mm]\,[rr]\,/\,[mr]^2$$

has values near to the unit, generally comprised in the range 0.7-1.3, preferably comprised in the range 0.8-1.2.

[0045] In the process of the invention, the polymerization reaction of propylene can b carried out in the presence of one or more olefins selected between ethylene and the α-olefins containing from 4 to 20 carbon atoms. Non limitative

xamples of these α-olefins are 1-butene, 1-pentene, 1-hexene, 1-octene and 1,5-hexadiene.

[0046] In particular, with the process of th present invention it is possible to prepare substantially amorphous copolymers of propylene with small quantities, that is up to about 10% by mole, of comonomeric units.

[0047] The possibility of obtaining directly, as the only product of the polymerization reaction of propylene, a substantially amorphous polypropylen endowed with high molecular weight represent an advantage over the traditional processes.

[0048] The process of the polymerisation of olefins according to the invention may be carried out in liquid phase, optionally in the presence of an inert hydrocarbon solvent, or in gas phase. The hydrocarbon solvent may be aromatic such as toluene, or aliphatic, such as propane, hexane, heptane, isobutane, cyclohexane.

[0049] The polymerisation temperature is generally comprised between -100°C and +80°C, and more preferably between -50°C and +50°C. The lower the polymerisation temperature, the higher the molecular weight of the polymer obtained results.

[0050] In particular, by the process of the invention propylene polymers may be obtained having molecular weights of industrial interest at relatively high temperatures. The molecular weight of the polymers obtained in the presence of the catalysts of the invention are in any case higher with respect to those polymers obtained with the corresponding catalysts in which the indenyl group of the metallocene compound is not substituted in the 2-position.

[0051] The molecular weight of the polymer may be in addition varied, by varying the type or concentration of the catalytic components or by using molecular weight regulators such as, for example, hydrogen.

[0052] The molecular weight distribution may be varied by using mixtures of different metallocene, or by carrying out the polymerization in more steps which differ in the polymerization temperature and/or the concentration of the molecular weight regulator.

[0053] The polymerization yield depends on the purity of the metallocene component of the catalyst. Moreover the metallocene compound obtained by the process of the invention may be used as such or undergo purification treatment.

[0054] The different catalyst components may be put into contact before the polymerisation. The contact time is generally comprised between 1 and 60 minutes, preferably between 5 and 20 minutes. The concentration of the precontact for the metallocene component (A) are comprised between 10^{-2} and 10^{-8} mol/l, while for component (B) are comprised between 10 and 10^{-3} mol/l. The precontact is generally carried out in the presence of a hydrocarbon solvent and, optionally, small quantities of monomer.

[0055] The following examples are given to illustrate the invention and not to limit it.

CHARACTERISATIONS

[0056] The intrinsic viscosity [η] is measured in tetraline at 135°C.

[0057] The Differential Scanning Calorimetry (DSC) have been carried out on a DSC-7 instrument by Perkin Elmer Co. Ltd. according to the following process. Approximately 10 mg of sample is heated to 180°C, with a scanning speed equal to 1-0°C/minute; The sample is maintained at 180°C for 5 minutes and then cooled at a scanning speed equal to 10°C/minute. Then a second scanning is carried out in the same way as the first. The values reported are those from the second scanning.

[0058] The ^{13}C-N.M.R. analysis of the polymer have been carried out on Bruker AC200 instrument at 50.323 MHz, using $C_2D_2Cl_4$ as solvent (about 300 mg of dissolved polymer in 2,5 ml of solvent), at a temperature of 120°C.

[0059] The ^{1}H-N.M.R. analysis of the polymer have been carried out on a Bruker AC200 instrument at 200.133 MHz, using $CDCl_3$ as solvent at room temperature.

[0060] The gas-chromatographic analysis (GC) have been carried out with a Hewlett-Packard Gas Cromatograph (5890 Series II) with a HP5 column (5% phenyl methyl silicon) of 50 meters, 0.22 i.d., film thickness 0.5 μm. It has been worked in a temperature range of from 30 to 300°C, with a gradient of 4°C/minute, with an initial isotherm of 4 minutes. The injector was on the column (1 μl of sample dissolved in THF or CH_2Cl_2).

PREPARATION OF THE METALLOCENE

[0061] All the operations have been carried out under an inert atmosphere.

THF	= tetrahydrofuran
Et_2O	= diethyl ether

EXAMPLE 1

BIS(2-METHYL-INDENYL)ZIRCONIUM DICHLORIDE

(a) Synthesis of 2-methyl-2-indanol

[0062] A solution of 36 g of 2-indanone (distilled before use) in 400 ml of anhydrous Et_2O was slowly added to a mixture of methyl magnesium bromide (100ml of a 3M solution in hexane) in 200 ml of Et_2O at 0°C.

[0063] The mixture was stirred at room temperature. After 3 hours the reaction was stopped with 350 g of ice and a solution of 30 g of NH_4Cl in 500 ml of water. The organic layer was separated, washed with 500 ml of a saturated solution of $NaHCO_3$ and then 500 ml of water, dried on sodium sulphate and concentrated under vacuo.

[0064] 37,8 g of a clear yellow solid was obtained identified as 2-methyl-2-indanol by N.M.R. and GC-MS analysis.

(b) Synthesis of 2-methyl-indene

[0065] 1 g of p-toluene-sulphonic acid monohydrate and 25 g of the product obtained at point (a) were dissolved in 100 ml of toluene. The solution obtained was maintained under reflux for 2 hours. GC analysis of the reaction crude indicated at this point that the conversion to 2-methyl-indene was 96%. The solution was concentrated under vacuo and then distilled in the presence of a small amount of 4-t-butyl-catechol and of 2 drops of NaOH. 16.7 g of 2-methyl-indene was obtained having boiling point of 58-60°C at 2 mm Hg.

[0066] ^{1}H-N.M.R. ($CDCl_3$), δ(ppm): 7.4-7.0 (m, 4 H), 6.11 (s, 1 H), 3.21 (s, 2 H), 2.10 (s, 3 H).

(c) Synthesis of bis(2-methyl-indenyl)zirconium dichloride

[0067] 4,4 ml of a solution 2.5M of n-butyllithium in hexane were added to a solution of 1.42 g of 2-methyl-indene obtained at point (b), dissolved in 30 ml of THF at 0°C. After the addition the solution was left to return to room temperature and maintained under stirring for a further 4 hours. The volatile substances were removed under vacuo and the solid so obtained was washed with pentane.

[0068] 1.27 g of $ZrCl_4$ in powder form was added to this solid and the whole was suspended in pentane. In order to facilitate the reaction, 1 ml of THF was added. The suspension was maintained under stirring overnight and at the end the solid was separated by filtration and washed with pentane.

[0069] The product so obtained was dissolved in CH_2Cl_2, filtered, and the solution dried. 1,51 g of a yellow powder was so obtained identified as bis(2-methyl-indenyl)zirconium dichloride from its ^{1}H-N.M.R. spectrum.

[0070] ^{1}H-N.M.R. ($CDCl_3$), δ (ppm): 7.75-7.55 (m, 4 H, Ar), 7.35-7.15 (m, 4H, Ar), 5.81 (s, 4 H, H1 e H3), 2.04 (s, 6 H, Me).

EXAMPLE 2 (comparison)

BIS(INDENYL)ZIRCONIUM DICHLORIDE

[0071] 7.0 ml (60 mmols) of indene were dissolved in 20 ml of anhydrous THF, the solution was cooled to -78°C and treated with 40.0 ml of n-butyllithium (1.5 M in hexane, 60 mmols). It was left to warm to room temperature thus obtaining a red coloured solution.

[0072] In a 100 ml round-bottomed flask provided with reflux cooler, 7 g of $ZrCl_4$ (30 mmols) were cooled to -78°C and treated with 30 ml of THF (exothermic reaction). Thereafter, the whole was heated under reflux for 30 minutes, until a clear, brown coloured solution was obtained.

[0073] The solution of indenyl lithium was added, at room temperature, to the solution of the $ZrCl_4$/THF adduct. It was kept stirred for 2 hours (a yellow suspension was formed) and thereafter the solvent was completely evaporated.

[0074] The residue was suspended in Et_2O filtered off, washed repeatedly with Et_2O and extracted with dichloromethane.

[0075] The solution was dried and the product was washed with Et_2O and then with pentane: 4.35 g of bis(indenyl) zirconiumdichloride were thus obtained (36.8%).

EXAMPLE 3

BIS(2,4,7-TRIMETHYL-INDENYL)ZIRCONIUM DICHLORIDE

(a) Synthesis of 2,4,7-trimethyl-indan-1-one

[0076] 80 mL of CH_2Cl_2 and 19 g of $AlCl_3$ (Aldrich) were placed in a 250 mL, 3-neck round bottomed flask equipped with magnetic stirring bar, 100 mL dropping funnel, thermometer and reflux condenser. The flask was placed in a Dewar and cooled to 0 °C. A solution of 7.7 mL of methacryloyl chloride (Aldrich, 90%) and 8.7 mL of p-xylene (Aldrich) in 50 mL of CH_2Cl_2 was placed in the dropping funnel and added dropwise to the stirred $AlCl_3/CH_2Cl_2$ slurry over 2 hours at 0 °C. A red slurry was obtained, which was allowed to warm to room temperature and stirred overnight (18 hours). The slurry was then poured into a flask containing 100 mL of 37 % HCl and 100 g of ice. The solids were decanted off, the organic layer separated, the aqueous layer extracted with Et_2O (3x100 mL). The combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$ and then water, dried over Na_2SO_4, filtered and evaporated to leave 12.75 g of a yellow-orange oil, containing 54 % 2,4,7-trimethyl-indan-1-one and 19.9 % dimers (GC). Yield based on GC purity 56 %. This product was used without any further purification.

(b) Synthesis of 2,4,7-trimethyl-indan-1-ol

[0077] 2.7 g of $LiAlH_4$ and 250 mL Et_2O were placed in a 3-neck 500 mL round bottomed flask equipped with magnetic stirring bar, reflux condenser and 100 mL dropping funnel. A 100 mL solution of 12.73 g of the product obtained at point (a) in Et_2O was placed in the dropping funnel and added dropwise at room temperature over 1 hour in the stirred $LiAlH_4/Et_2O$ slurry. At the end of the addition, the slurry was refluxed for two hours, then cooled with an ice water bath. Subsequently, 5 mL of H_2O, 5 mL of a 10 % NaOH solution and again 5 mL of H_2O were slowly added, the slurry was filtered and the filtrate dried over Na_2SO_4, filtered and evaporated on the rotavac to leave 12.053 g of a straw-yellow oil. GC analysis shows the presence of the two diastereomers of 2,4,7-trimethyl-indan-1-ol (38.5% and 20.1%).

(c) Synthesis of 2,4,7-trimethyl-indene

[0078] 12.0 g of the product obtained at point (b), 75 mg of p-toluene sulfonic acid and 150 mL of toluene were placed in a 250 mL round bottomed flask equipped with magnetic stirring bar. The solution was heated to 80 °C for 15 minutes, then treated with a saturated $NaHCO_3$ aqueous solution. The organic layer was separated, washed with water, dried over Na_2SO_4 and evaporated in vacuo to leave 8.68 g of an orange oil. This oil was vacuo-distilled to yield 4.5 g of a straw-yellow solid. GC analysis: 2,4,7-trimethylindene 92.4 %.

[0079] ^{1}H-N.M.R. ($CDCl_3$), δ(ppm): 6.97 (d, J=7.6 Hz, 1 H, Ar), 6.84 (d, J=7.6 Hz, 1 H, Ar), 6.62-6.58 (m, 1 H, H3), 3.20 (bs, 2 H, H1), 2.37 (s, 3 H, Me), 2.30 (s, 3 H, Me), 2.19 (s, 3 H, Me2?).

[0080] This product was used without any further purification.

(d) Synthesis of bis(2,4,7-trimethyl-indenyl)zirconium dichloride

[0081] A solution of 4.0 g of the 2,4,7-trimethylindene obtained at point (c) in 20 ml THF was added dropwise to a suspension of 1.04 g KH in 80 ml THF at room temperature. H_2 evolution was observed. At the end of the addition the mixture was stirred until gas evolution ceased (2 hours). The remaining solid was decanted off and the dark brown liquid was transferred into a 100 ml dropping funnel and added dropwise into a flask containing a rapidly stirring solution of 4.4 g of $ZrCl_4(THF)_2$ in 50 ml THF. During the addition a green-yellow suspension was obtained. After stirring at room temperature for 2 hours (yellow suspension) the volume of the slurry was concentrated to 10 ml and an equal volume of Et_2O was added. The mixture was stirred for a few minutes and filtered. The filtrate was cooled to -20 °C for 2 days, and 1.10 g of solid precipitated and were isolated by filtration (A). The yellow solid was washed with 5 mL HCl 4N, 5 mL H_2O, 5 mL EtOH and 2x5 mL Et_2O. After drying, 1.48 g of a bright yellow solid were obtained (B). The two solid fractions (A) and (B) were combined and continuously extracted with CH_2Cl_2 (80 mL, 2 hours), then dried, yielding 2.02 g of $(2,4,7\text{-trimethyl-indenyl})_2ZrCl_2$ pure by ^{1}H-N.M.R. (yield 35 %).

[0082] ^{1}H-N.M.R. ($CDCl_3$), δ(ppm): 6.86 (s, 4 H, H5 e H6), 6.36 (s, 4 H, H1 e H3), 2.44 (s, 12 H, Me4 eMe7), 2.14 (s, 6 H, Me2).

EXAMPLE 4 (mparison)

BIS(4,7-DIMETHYL-INDENYL)ZIRCONIUM DICHLORIDE

(a) Synthesis of 4,7-dimethyl-indan-1-one

[0083] 180 mL CH_2Cl_2 and 36 g anhydrous $AlCl_3$ (Carlo Erba) were charged in a 3-neck 0.5-L round bottomed flask equipped with magnetic stirring bar, 250-ml dropping funnel, thermometer and reflux condenser. A solution containing 31 ml p-xylene and 21 ml acryloylchloride (Aldrich) in 100 ml CH_2Cl_2 was placed in the dropping funnel. This solution was added dropwise over 4 hours to the flask, the content of which was kept under stirring at the temperature of 0°C with a bath of water and ice. Evolution of HCl was observed and the reaction mixture turned dark brick-red. After addition was complete, the mixture was allowed to warm to room temperature and stirring was continued overnight (18 hours). The reaction mixture was poured in a flask containing 250 g ice and 250 ml HCl 37 %, the organic phase was separated and the acqueous phase was extracted with Et_2O (3 times). All organic fractions were combined and washed with saturated aqueous $NaHCO_3$ and water, dried with Na_2SO_4, filtered and the solvent was removed in vacuo. 38.25 g of light yellow-orange oil were obtained. This product was used without any further purification.

(b) Synthesis of 4,7-dimethyl-indan-1-ol

[0084] 3.0 g of $LiAlH_4$ and 300 ml anhydrous THF were placed in a 3-neck 1 liter round bottomed flask equipped with magnetic stirring bar, 250 mL dropping funnel and reflux condenser. A 250 mL solution of 38.25 g of the product obtained at point (a) in THF was placed in the dropping funnel. This solution was added dropwise at room temperature over 1 hour to the flask the content of which was kept under stirring. At the end of the addition, the slurry was refluxed for 1.5 hours, then cooled with an ice water bath. Subsequently, 10 mL of H_2O, 10 mL of a 15 % NaOH solution and again 10 mL of H_2O were slowly added. The obtained slurry was filtered and the filtrate dried over Na_2SO_4, then filtered and evaporated to leave 40.16 g of a dark-red oil.

(c) Synthesis of 4,7-dimethyl-indene

[0085] All the product obtained at point (b), 350 mg of p-toluen-sulfonic acid and 400 mL of benzene were placed in a 3-neck 500 mL round bottomed flask equipped with magnetic stirring bar and of a device for azeotropes collection. The obtained solution was heated for 15 minutes up to benzene reflux, then treated with a saturated $NaHCO_3$ aqueous solution. The organic layer was separated, washed with water, dried over Na_2SO_4, filtered and evaporated in vacuo to leave 28.854 g of a viscous dark-brown oil. This oil was vacuo-distilled to yield 12.3 ml of a clear colorless liquid, identified as 4,7-dimethylindene by its ^{1}H-N.M.R. spectrum.

(d) Synthesis of bis(4,7-dimethyl-indenyl)zirconium dichloride

[0086] A solution of 5.8 g of 4,7-dimethylindene obtained at point (c) in 30 ml THF was added dropwise to a suspension of 1.8 g KH in 90 ml THF at room temperature. H_2 evolution was observed. At the end of the addition the mixture was stirred until gas evolution ceased (1.5 hours). The remaining solid was decanted off and the green-brown liquid was transferred into a 250 ml dropping funnel and added dropwise into a flask containing a rapidly stirring solution of 7.12 g of $ZrCl_4(THF)_2$ in 55 ml THF. During the addition the formation of a bulky yellow precipitate was observed. Additional 80 ml of THF were added to facilitate stirring. After stirring at room temperature for 2 hours, the volume of the suspension was concentrated to 60 ml and an equal volume of Et_2O was added. The mixture was stirred for a few minutes and filtered. The yellow solid was continuously extracted with CH_2Cl_2 for 20 hours, then dried, yielding 7.15 g of a lemon-yellow solid identified as bis(2,4,7-trimethyl-indenyl)zirconium dichloride by its ^{1}H-N.M.R. spectrum.

[0087] ^{1}H-N.M.R. ($CDCl_3$), δ(ppm): 6.96 (s, 4 H, H5 e H6), 6.48 (t, J=3.4 Hz, 2 H, H2), 6.24 (d, J=3.4, 4 H, H1 e H3) 2.43 (s, 12 H, Me)

EXAMPLE 5

BIS(2,4,6-TRIMETHYL-INDENYL)ZIRCONIUM DICHLORIDE

(a) Synthesis of 2,5,7-trimethyl-indan-1-one

[0088] 160 mL of CH_2Cl_2 and 38 g of $AlCl_3$ (Aldrich) were placed in a 500 mL, 3-neck round bottomed flask equipped with magnetic stirring bar, 250 mL dropping funnel, thermometer and reflux condenser. The mixture was cooled to 0

°C. A solution of 15.4 mL of methacryloyl chloride (Aldrich, 90%) and 17.4 mL of m-xylene (Aldrich) in 100 mL of CH_2Cl_2 was placed in the dropping funnel and added dropwise to the stirred $AlCl_3/CH_2Cl_2$ slurry over 2 hours at 0 °C. A red slurry was obtained, which was allowed to warm to room temperature and stirred overnight (18 hours). The slurry was then poured into a flask containing 200 mL of 37 % HCl and 200 g of ice. The solids were decanted off, the organic layer separated, the aqueous layer extracted three times with Et_2O. The combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$ and then water, dried over Na_2SO_4, filtered and evaporated to leave 26.13 g of dark green liquid, containing 83.2 % 2,5,7-trimethyl-indan-1-one and 11.3 % dimers (GC). Yield based on GC purity 89 %. This product was used without any further purification.

(b) Synthesis of 2,5,7-trimethyl-indan-1-ol

[0089] 6.13 g of $LiAlH_4$ and 250 mL Et_2O were placed in a 3-neck 500 mL round bottomed flask equipped with magnetic stirring bar, reflux condenser and 100 mL dropping funnel. A 100 mL solution of 26.13 g of the product obtained at point (a) in Et2O was placed in the dropping funnel and added dropwise at room temperature over 40' in the stirred $LiAlH_4/Et_2O$ slurry. At the end of the addition, the slurry was refluxed for two hours, then cooled with an ice water bath. Subsequently, 5 mL of H_2O, 5 mL of a 10 % NaOH solution and again 5 mL of H_2O were slowly added, the slurry was filtered and the filtrate dried over Na_2SO_4, filtered and evaporated on the rotavac to leave 25.28 g of a yellow oil which solidifies upon cooling. GC analysis shows the presence of the two diastereomers of 2,5,7-trimethyl-indan-1-ol.

(c) Synthesis of 2,4,6-trimethyl-indene

[0090] 25.03 g of the product, obtained at point (b) 75 mg of p-toluen-sulfonic acid and 150 mL of toluene were placed in a 250 mL round bottomed flask equipped with magnetic stirring bar. The solution was heated at 80 °C for 15', then treated with a saturated $NaHCO_3$ aqueous solution and the organic layer separated, washed with water, dried over Na_2SO_4 and evaporated in vacuo to leave 23.35 g of an orange oil. GC analysis: 2,4,6-trimethylindene 86.9 %. This product was used in the next step without any further purification.

(d) Synthesis of bis(2,4,6-trimethyl-indenyl)zirconium dichloride

[0091] A solution of 4.0 g of 2,4,6-trimethylindene obtained at point (c) in 20 ml THF was added dropwise to a suspension of 0.98 g KH in 80 ml THF at room temperature. H_2 evolution was observed. At the end of the addition the mixture was stirred until gas evolution ceased (2 hours). The remaining solid was decanted off and the dark brown liquid was transferred into a 100 ml dropping funnel and added dropwise into a flask containing a rapidly stirring solution of 4.14 g of $ZrCl_4(THF)_2$ in 50 ml THF. During the addition a brown-yellow suspension was obtained. After stirring at room temperature for 2 hours (yellow suspension) the volume of the slurry was concentrated to 10 ml and 20 mL of Et_2O was added. The mixture was stirred for a few minutes and filtered. The filtrate was cooled to -20 °C, and 0.825 g of solid precipitated and were isolated by filtration (A). The yellow solid was washed with 5 mL HCl 4N, 5 mL H_2O, 5 mL EtOH and 2x5 mL Et_2O. After drying, 1.854 g of bright yellow solid were obtained (B). The two solid fractions (A) and (B) were combined and continuously extracted with CH_2Cl_2 (80 mL, 4 hours), then dried, yielding 1.874 g of $(2,4,6\text{-trimethyl-indenyl})_2ZrCl_2$ (pure by ^1H NMR, 1:1 mixture of its two isomers).

EXAMPLE 6 (comparison)

BIS(4,6-DIMETHYL-INDENYL)ZIRCONIUM DICHLORIDE

(a) Synthesis of 5,7-dimethyl-indan-1-one

[0092] 150 mL of CH_2Cl_2 and 72 g of $AlCl_3$ (Aldrich) were placed in a 500 mL, 3-neck round bottomed flask equipped with magnetic stirring bar, 250 mL dropping funnel, thermometer and reflux condenser. The flask was placed in a Dewar and cooled to 0 °C. A solution of 21 mL of acryloyl chloride (Aldrich, 98%) and 31 mL of m-xylene (Aldrich) in 100 mL of CH_2Cl_2 was placed in the dropping funnel and added dropwise to the stirred $AlCl_3/CH_2Cl_2$ slurry over 2 hours (hexothermic reaction with HCl evolution). A red-orange slurry was obtained, which was allowed to warm to room temperature and stirred overnight (18 hours). The slurry was then slowly poured into a flask containing 200 mL of 37 % HCl and 200 g of ice. The solids were decanted off, the organic layer separated, th aqueous layer extracted three times with Et_2O. The combined organic layers wer washed with a saturated aqueous solution of $NaHCO_3$ and then water, dried over Na_2SO_4, filtered and evaporated on the rotavac to leave 41.06 g of an oil, containing 58.65 % 5,7-dimethyl-indan-1-one identified by GC. Yield 60 %. This product was used in the next step without any further purification.

(b) Synthesis of 5,7-dimethyl-indan-1-ol

[0093] 5.1 g of $LiAlH_4$ and 250 mL Et_2O were placed in a 3-neck 2-L round bottomed flask equipped with magnetic stirring bar, reflux condenser and 250 mL dropping funnel. A 250 mL solution of 41 g of the product obtained at point (a) in Et_2O was placed in the dropping funnel and added dropwise at room temperature over 80' in the stirred $LiAlH_4$/Et_2O slurry. At the end of the addition, the slurry was refluxed for two hours, then cooled with an ice water bath. Subsequently, 10 mL of H_2O, 10 mL of a 15 % NaOH solution and again 10 mL of H_2O were slowly added, the slurry was filtered and the filtrate dried over Na_2SO_4, filtered and evaporated on the rotavac to leave 44.60 g of a yellow oil which solidifies upon cooling. GC analysis confirms the presence of 57% 5,7-dimethyl-indan-1-ol. The product was used in the next step without any further purification.

(c) Synthesis of 4,6-dimethyl-indene

[0094] 44.036 g of the product obtained at point (b), 350 mg of p-toluen-sulfonic acid and 400 mL of toluene were placed in a 1-L round bottomed flask equipped with magnetic stirring bar and reflux condenser. The solution was heated at 80 °C for 15', then treated with a saturated $NaHCO_3$ aqueous solution and the organic layer separated, washed with water, dried over Na_2SO_4 and evaporated in vacuo to leave 35.425 g of a yellow-orange oil. 33.86 g of this oil was distilled on a 10 cm Vigreux column (62-63 °C, 0.7 mmHg) in the presence of NaOH. 17 ml of a yellow liquid were recovered. GC analysis: 4,6-dimethylindene 95.0%. The product was used in the next step without any further purification.

(d) Synthesis of bis(4,6-dimethyl-indenyl)zirconium dichloride

[0095] 7.0 g of 4,6-dimethylindene obtained at point (c) in 30 ml THF was added dropwise to a suspension of 2.05 g KH in 90 ml THF at room temperature. H_2 evolution was observed. At the end of the addition the mixture was stirred until gas evolution ceased (2 hours). The remaining solid was decanted off and the dark green liquid was transferred into a 250 ml dropping funnel and added dropwise into a flask containing a rapidly stirring solution of 8.69 g of $ZrCl_4$ $(THF)_2$ in 80 ml THF. During the addition the solution becomes cloudy orange. After stirring at room temperature for 2 hours (a yellow slurry was formed) the volume of the slurry was concentrated to 10 ml and an equal volume of Et_2O was added. The mixture was stirred for a few minutes and filtered. The yellow solid was washed with 10 mL HCl 4N, 10 mL H_2O, 5 mL EtOH and Et_2O (5x2 + 12x2 mL) and finally dried, yielding 6.72 g of a yellow solid identified as bis (4,6-dimethyl-indenyl)zirconium dichloride by ^{1}H-NMR analys.

EXAMPLE 7 (comparison)

BIS(2-T-BUTYL-INDENYL)ZIRCONIUM DICHLORIDE

(a) Preparation of 2-isopropylidene-1-indanone

[0096] To a solution of 1-indanone (120 g, 0.908 mole) in acetone (180 g) inside of 500 mL round-bottom flask was added 9 mL of ethanolic potassium hydroxide (3 g, 0.054 mole) solution. The solution was heated under reflux for 7.5 hours and then acidified with acetic acid. Volatile components were removed by a rotary evaporator. To the residue diethyl ether (200 mL) and water (100 mL) were added. The aqueous layer was extracted with diethyl ether (4 * 200 mL). All etheral layers were combined, washed with water (50 mL), dried over anhydrous magnesium sulfate and concentrated to yield 152 g of crude product. Fractional distillation (80 to 120°C/0.3 mmHg) and recrystallization from methanol yielded 29 g of 2-isopropylidene-1-indanone. H-NMR ($CDCl_3$) δ 1.99 (s, 3 H), 2.43 (s, 3 H), 3.62 (s, 2 H), 7.36 (br t, J=7.6 Hz, 1 H), 7.45 (br d, J=7.6 Hz, 1 H), 7.53 (td, J= 7.6, 1.2 Hz, 1H), 7.80 (br d, J= 7.6 Hz, 1H).

(b) Preparation of 2-t-butyl-1-indanone

[0097] To the cupurous chloride (0.258 g, 2.61 mmol) inside 250 mL round bottom flask was added 22 mL of methylmagnesium iodide (3.0 M solution in diethyl ether, 66 mmol) at 0°C under nitrogen. Diethyl ether was removed in vacuo. Tetrahydrofuran (65 mL) was then introduced. To this resulting suspension was added a solution of 2-isopropylidene-1-indanone (5.00 g, 29 mmol) in Tetrahydrofuran (25 mL) through a dropping funnel dropwise at 0°C. The mixture was stirred at the same temperature for another 1 h and then at ambient temperature overnight (16 h). The slurry was poured into ice (32 g) containing ammonium chloride (6.44 g). The solution was extracted with diethyl ether (5 * 80 mL). All ethereal layers were combined, washed with water (20 mL), dried over anhydrous magnesium sulfate and concentrated to yield 5.29 g (97%) of 2-t-butyl-1-indanone. H-NMR ($CDCL_3$) 6 0.95 (s, 9H), 2.38 (dd, J= 4.3, 8.0

Hz, 1 H), 2.90 (dd, J= 4.3, 17.4 Hz, 1H), 3.08 (dd, J=8.0, 17.4 Hz, 1H) 7.23 (br t, J=7.4 Hz, 1H), 7.35 (br d, J=7.6 Hz, 1H), 7.46 (br t, J=7.6 Hz, 1H), 7.61 (br d, J=7.4 Hz, 1H):

(c) Preparation of 2-t-butyl-1-indanol

[0098] To a suspension of lithium aluminium hydride (1.164 g, 30.7 mmol) in anhydrous diethyl ether (100 mL) was added a solution of 2-t-butyl-1-indanone (8.32 g, 49.6 mmol) in anhydrous diethyl ether (100 mL) under nitrogen. The mixture was stirred at ambient temperature overnight (16 h). Water (1.2 mL), 15% aqueous sodium hydroxide (1.2 mL), water (3.5 mL) were added consequently. Solid was filtered off and washed with ether (200 mL). Etheral solution was dried over anhydrous magnesium sulfate and concentrated to yield 8.19 g (87%) of 1:1 mixture of diastereomers of 2-t-butyl-1-indanol. ^{1}H-NMR ($CDCL_3$) 6 1.02(s), 1.16 (s, overlapping a broad singlet at 1.16, total 10 H), 1.96-2.10 (m. 1H), 2.64-2.84 (m, 1H), 2.95-3.10 (m, 1H), 5.00-5.15 (m, 1H), 7.16-7.28 (m, 3 H), 7.35-7.40 (m, 1H).

(d) Preparation of 2-t-butyl-indene

[0099] A solution of 2-t-butyl-1-indanol (8.19 g, 43.1 mmol) and p-toluenesulfonic acid (0.200 g, 1.05 mmol) in benzene was heated under reflux for 0.5 h. Water (20 mL) was added. Aqueous layer was extracted with ether (4 * 50mL). All organic layers were combined, washed with water (20 mL), brine (10 mL) and concentrated to produce 7.41 g (100 g) of 2-t-butylindene. ^{1}H-NMR ($CDCl_3$) δ 1.18 (s, 9 H), 3.30 (s, 2H), 6.45 (s, 1H), 7.02 (tdd, J=7.3, 1.4, 0.3 Hz, 1H), 7.14 (br t, J=7.5 Hz, 1H), 7.19 (br d, J=7.3 Hz, 1H), 7.31 (br d, J=7.3 Hz, 1 H). ^{13}C-NMR ($CDCl_3$) 6 30.44, 33.45, 37.84, 120.09, 123.42, 123.50, 123.63, 126.25, 143.11, 145.49, 150.16.

(e) Synthesis of 2-t-butyl-indenyl-zirconium dichloride.

[0100] 3.13 g of 2-t-butyl-indene in 50 mL THF were added dropwise to 0.81 g of KH in 170 mL THF. At the end of the addition the suspension was stirred for 2 hours at room temperature. Excess KH was decanted off and the yellow-green solution was added dropwise (3 h) to a solution of 3.42 g of $ZrCl_4(THF)_2$ in 70 mL THF. The yellow suspension was stirred for additional 18 hours, then concentrated in vacuo to a volume of approximately 10 mL, and 40 mL of Et_2O were added. The slurry was stirred for a few minutes, then filtered, and the solid was washed with Et_2O until the washing was colourless. A white solid, soluble in water, was left on the frit, and was discarded. All ethereal fractions were combined and dried in vacuo, to give a sticky solid which was washed with hexane until a lemon-yellow, free flowing powder was obtained, which was dried in vacuo (1.63 g). This product was (2-t-butylindenyl)$_2$$ZrCl_2$ pure by ^{1}H-NMR. Yield 36%.

^{1}H-NMR (δ, ppm, $CDCl_3$): 7.7-7.8 (m, 4H), 7.2-7.3 (m, 4H), 5.85 (s, 4H) and 1.0 (s, 18H).

EXAMPLE 8

BIS(2-METHYL-4,5,6,7-TETRAHYDROINDENYL)ZIRCONIUM DICHLORIDE

[0101] 0.768 g of the bis(2-methyl-indenyl)zirconium dichloride obtained in Example 1 and 45 ml CH_2Cl_2 were charged in a 50 ml test-tube. The mixture was kept under stirring for 5 minutes at room temperature and to the obtained yellow suspension 25 mg of PtO_2 were added. The resulting suspension was then transferred into a 100 ml autoclave. After substitution of the nitrogen atmosphere with an hydrogen atmosphere and rising the pressure to 5 atm. The system was left under stirring for 4 hours at room temperature. At the end of the reaction the catalyst was removed by filtration. The filtrate was concentrated until complete removal of the solvent, thus obtaining 0.603 g of a white solid identified as bis(2-methyl-4,5,6,7-tetrahydroindenyl)zirconium dichloride by ^{1}H-N.M.R. analysis.

POLYMERIZATION OF PROPYLENE

Methylalumoxane (MAO)

[0102] A commercial (Schering, MW 1400) 30% toluene solution of MAO was used. After having removed the volatile fractions under vacuo, a solid glassy material was finely crushed and further treated in vacuo (0.1 mmHg) for 4-6 hours, at a temperature of 40-50°C to leave a white powder.

Modified methylalumoxan (M-MAO)

[0103] The commmercial (Ethyl) isopar C solution (62 g Al/L) was used as received.

EXAMPLES 9-10

[0104] A 1.4 l ste l autoclave equipped with a magnetic stirrer. manometer, temperature indicator, a 35 ml barrel for loading the catalyst, a feed line for the monomers, a forced circulation thermostating jacket, and a control for the synthesis conditions by means of an automatic computerised system was used.
[0105] Into the autoclave, which had been previously washed with gaseous propylene at about 70°C, and brought to the reaction temperature indicated in Table 1, 1.0 1 of liquid propylene was loaded.
[0106] The catalyst solution was prepared by pre-contacting the amounts of MAO and bis(2-methyl-indenyl)zirconium dichloride indicated in Table 1 in 10 ml of toluene, for 10 minutes at room temperature.
[0107] The catalyst solution was fed into the autoclave through the barrel under pressure of pure nitrogen. After the reaction time indicated in Table 1 at a constant temperature, the non-reacted monomer was degassed and the product so obtained was dried under nitrogen in an oven under vacuo at 60°C.
[0108] The polymerization conditions and the characterisation data of the obtained polymer are reported in Table 1. From DSC analysis no peaks were observed attributable to the melt enthalpy.

EXAMPLES 11-14

[0109] It was worked according to the procedure described in the examples 9-10, but using a 1.0 l steel autoclave equipped with a magnetic stirrer, manometer, temperature indicator, a barrel for loading the catalyst, a feed line for the monomers and a forced circulation thermostating jacket, and loading 0.4 l of liquid propylene.
[0110] The polymerization conditions and the characterisation data of the polymer obtained are reported in table 1. From DSC analysis, no peaks were observed attributable to the melt enthalpy.

EXAMPLES 15-18

[0111] It was worked according to the procedure described in the examples 9-10, but using a 1.0 l glass autoclave equipped with a magnetic stirrer, manometer, temperature indicator, a barrel for loading the catalyst, a feed line for the monomers and a forced circulation thermostating jacket, and loading 0.4 l of liquid propylene.
[0112] The polymerization conditions and the characterisation data of the polymer obtained are reported in table 1. From DSC analysis, no peaks were observed attributable to the melt enthalpy.

EXAMPLE 19 (COMPARISON)

[0113] It was worked according to the procedure described in the examples 9-10, but using bis(indenyl)zirconium dichloride instead of bis(2-methyl-indenyl)zirconium dichloride.
[0114] The polymerization conditions and the characterisation data of the polymer obtained are reported in table 1. From DSC analysis, no peaks were observed attributable to the melt enthalpy.

EXAMPLES 20-22 (COMPARISON)

[0115] It was worked according to the procedure described in the examples 11-14, but using bis(indenyl)zirconium dichloride instead of bis(2-methyl-indenyl)zirconium dichloride.
[0116] The polymerization conditions and the characterisation data of the polymer obtained are reported in table 1. From DSC analysis, no peaks were observed attributable to the melt enthalpy.

EXAMPLE 23

[0117] It was worked according to the procedure described in the examples 9-10, but using bis(2,4,7-trimethyl-indenyl)zirconium dichloride instead of bis(2-methyl-indenyl)zirconium dichloride.
[0118] The polymerization conditions and the characterisation data of the polymer obtained are reported in table 1. From DSC analysis, no peaks were observed attributable to the melt enthalpy.

EXAMPLES 24 (COMPARISON)

[0119] It was worked according to the procedure described in the examples 9-10, but using bis(4,7-dimethyl-indenyl) zirconium dichloride instead of bis(2-methyl-indenyl)zirconium dichloride.
[0120] The polymerization conditions and the characterisation data of the polymer obtained are reported in table 1. From DSC analysis, no peaks were observed attributable to the melt enthalpy.

EXAMPLE 25

[0121] It was worked according to the procedure described in the examples 9-10, but using bis(2,4,6-trimethyl-indenyl)zirconium dichloride instead of bis(2-methyl-indenyl)zirconium dichloride.

[0122] The polymerization conditions and the characterisation data of the polymer obtained are reported in table 1. From DSC analysis, no peaks were observed attributable to the melt enthalpy.

EXAMPLES 26 (COMPARISON)

[0123] It was worked according to the procedure described in the examples 9-10, but using bis(4,6-dimethyl-indenyl) zirconium dichloride instead of bis(2-methyl-indenyl)zirconium dichloride.

[0124] The polymerization conditions and the characterisation data of the polymer obtained are reported in table 1. From DSC analysis, no peaks were observed attributable to the melt enthalpy.

EXAMPLES 27

[0125] It was worked according to the procedure described in the examples 11-14, but using bis(2-methyl-4,5,6,7-tetrahydroindenyl)zirconium dichloride instead of bis(2-methyl-indenyl)zirconium dichloride.

[0126] The polymerization conditions and the characterisation data of the polymer obtained are reported in table 1. From DSC analysis, no peaks were observed attributable to the melt enthalpy.

EXAMPLES 28 (COMPARISON)

[0127] It was worked according to the procedure described in the examples 11-14, with the exception that the catalyst solution was prepared by pre-contacting, for 10 minutes at room temperature, 2.58 ml of M-MAO solution in isopar C (5.94 mmoles Al) with 1 mg of bis(2-t-butyl-indenyl)zirconium dichloride in 1 ml of toluene. No polymer was obtained.

[0128] The polymerization conditions are reported in table 1.

EXAMPLES 29 (COMPARISON)

[0129] It was worked according to the procedure described in example 28, but using 10 mg of bis(2-t-butyl-indenyl) zirconium dichloride in 5 ml of toluene. No polymer was obtained.

[0130] The polymerization conditions are reported in table 1.

TABLE 1

EXAMPLE	metallocene	Zr (μmoles)	Al/Zr (mol)	T (°C)	time (min)	yield (grams)	activity ($Kg_{pol}/mmol_{Zr}.h$)	I.V. (dL/g)	m-r (%)	B
9	$(2\text{-Me-Ind})_2ZrCl_2$	8.8	1000	50	60	57	6.5	0.26	7.72	0.98
10	"	8.8	1000	30	60	51	5.8	1.58	18.28	1.11
11	"	2.4	3000	30	60	9.5	4.0	1.45	n.a.	n.a.
12	"	2.4	3000	25	60	10.8	4.5	2.72	n.a.	n.a.
13	"	2.4	3000	20	15	9.2	15.0	4.18	19.60	1.13
14	"	2.4	3000	10	60	17.6	7.3	6.46	21.51	1.21
15	"	7.6	1000	0	60	61.4	8.0	11.43	17.60	1.28
16	"	1.2	3000	0	60	11.5	9.6	11.23	n.a.	n.a.
17	"	3.6	1000	-10	20	10.9	9.1	11.55	23.30	1.15
18	"	1.8	2000	-20	25	5.9	7.9	13.24	24.30	1.09
19 COMP.	$(Ind)_2ZrCl_2$	15.3	1000	50	120	278	9.0	liquid	n.a.	n.a.
20 COMP.	"	5.8	1400	50	60	105	18.0	liquid	8.4	8.4
21 COMP.	"	2.5	3000	20	60	11.9	4.7	0.63	7.93	1.01
22 COMP.	"	2.5	3000	0	60	4.7	1.8	1.82	11.9	0.9

EXAMPLE	metallocene	Zr (μmoles)	Al/Zr (mol)	T (°C)	time (min)	yield (grams)	activity ($Kg_{pol}/mmol_{Zr}.h$)	I.V. (dL/g)	m-r (%)	B
23	$(2,4,7\text{-}Me_3\text{-}Ind)_2ZrCl_2$	8.4	1000	50	60	33	3.9	liquid	29.28	1.07
24 COMP.	$(4,7\text{-}Me_2\text{-}Ind)_2ZrCl_2$	8.9	1000	50	120	3.5	0.2	liquid	n.a.	n.a.
25	$(2,4,6\text{-}Me_3\text{-}Ind)_2ZrCl_2$	8.4	3000	50	60	27.6	3.3	0.15	15.68	1.03
26 COMP.	$(4,6\text{-}Me_2\text{-}Ind)_2ZrCl_2$	8.9	3000	50	60	3.9	0.4	0.19	14.94	1.98
27	$(2\text{-}Me\text{-}H_4Ind)_2ZrCl_2$	9.8	1000	20	60	8.65	0.9	0.68	2.80	0.90
28 COMP.	$(2\text{-}tBu\text{-}Ind)_2ZrCl_2$	2.0	3000	50	60	0	-	-	-	-
29 COMP.	*	20.0	300	70	60	0	-	-	-	-

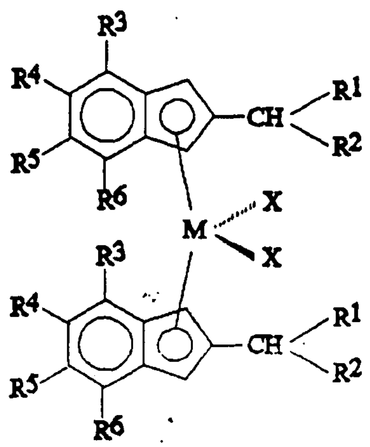
n.a. = not available

Claims

1. A process for the preparation of substantially amorphous polymers of propylene having melting enthalpies (ΔH_f) that are not measurable by differential scanning calorimetry comprising th polymerization reaction of propylene and optionally one or more olefins to obtain o homopolymer of propylene or o copolymer of propylene having up to 10% by mole of comonomeric units, said polymerization being carried out in th presence of a catalyst comprising

the product of the reaction between:

(A) a metallocene compound selected from the bis-indenyl compounds of formula (I):



(I)

and the corresponding bis-4,5,6,7-tetrahydroindenyl compounds, wherein:

on each indenyl or tetrahydroindenyl group the substituents R^1 and R^2, same or different from each other, are hydrogen atoms, $-CHR_2$ groups or -CHR-groups joined between them to form a cycle comprising from 3 to 8 carbon atoms, wherein the R substituents are hydrogen atoms, C_1-C_{20} alkyl radicals, C_3-C_{20} cycloalkyl radicals, C_2-C_{20} alkenyl radicals, C_6-C_{20} aryl radicals, C_7-C_{20} alkaryl radicals or C_7-C_{20} aralkyl radicals and can contain Si or Ge atoms;
the substituents R^3, R^4, R^5 and R^6, same or different from each other, are defined as R substituents, in addition two adjacent R^3, R^4, R^5 and R^6 substituents on the same ring can form a ring comprising from 5 to 8 carbon atoms;
M is a transition metal atom of groups IVb, Vb or VIb of the Periodic Table;
substituents X, same or different from each other, are hydrogen atoms, halogen atoms, $-R^7$, $-OR^7$, $-SR^7$,-NR^7_2 $-PR^7_2$ groups where substituent R^7 are defined as substituent R; and

(B) at least a compound selected among the organo-metallic compounds of aluminium containing at least an heteroatom selected from oxygen nitrogen and sulphur, and between the compounds able to give a metallocene alkyl cation.

2. The process according to claim 1, wherein the metallocene compound of formula (I) is present as the reaction product with an organometallic compound of aluminium of formula AlR^8_3 or $Al_2R^8_6$, wherein substituents R^8, same or different, are defined as substituent R or are halogen atoms.

3. The process according to claim 1 or 2 wherein, in each of the two indenyl or tetrahydroindenyl groups of the metallocene compound of formula (I), the substituents R^3 are the same as substituent R^6, while the substituents R^4 are the same as substituent R^5.

4. The process according to claim 3, wherein in the metallocene compound of formula (I) the substituents R^3, R^4, R^5 and R^6 are hydrogen atoms.

5. The process according to any of claims 1 to 4, wherein in the metallocene compound of formula (I) the transition metal M is selected from Ti, Zr or Hf.

6. The process according to any of claims 1 to 5, wherein in the metallocene compound of formula (I) the substituents X are chlorine atoms or methyl radicals.

7. The process according to any of claims 1 to 6, wherein in the metallocene compound of formula (I) the substituents R^1 are C_1-C_3 alkyl radicals.

8. The process according to claim 6, in which the substituents R^1 are methyl radicals.

9. The process according to any of claims 1 to 8, wherein the organo-metallic compound of aluminium containing at least an heteroatom is an alumoxane.

10. The process according claim 9, wherein the alumoxane is present as the reaction product with an organometallic compound of aluminium of formula AlR^8_3 or $Al_2R^8_6$, in which substituents R^8, same or different from each other, are defined ad substituents R or are halogen atoms.

11. The process according to claims 9 or 10, in which the alumoxane is methylalumoxane (MAO).

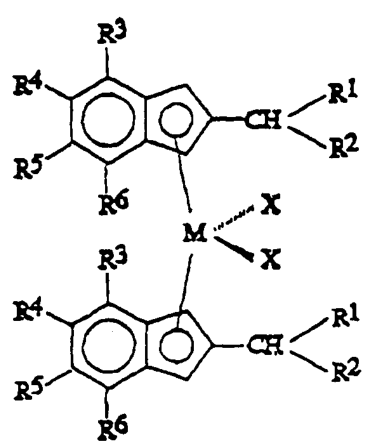
12. The process according to any of claims 9 to 11, wherein the molar ratio between the aluminium and the metal of the metallocene compound is comprised between 10:1 and 10000:1.

13. The process according to any of claims 1 to 12, wherein the polymerization reaction of propylene is carried out in the presence of one or more olefins selected between ethylene and the α-olefins containing from 4 to 20 carbon atoms.

Patentansprüche

1. Verfahren zur Herstellung von im wesentlichen amorphen Polymeren des Propylens mit Schmelzenthalpien (ΔHp), die durch Differentialscanningcalorimetrie nicht messbar sind, umfassend die Polymerisationsreaktion von Propylen und gegebenenfalls einem oder mehreren Olefinen zur Erzielung eines Homopolymeren von Propylen oder eines Copolymeren von Propylen mit bis zu 10 Mol% an Comonomereneinheiten, wobei diese Polymerisation in Gegenwart eines Katalysators durchgeführt wird, der das Reaktionsprodukt umfasst zwischen:

(A) einer Metallocenverbindung, ausgewählt unter Bis-indenylverbindungen der Formel (I):



(I)

und den entsprechenden Bis-4,5,6,7-tetrahydroindenylverbindungen, worin:

an jeder Indenyl- oder Tetrahydroindenylgruppe die Substituenten R^1 und R^2, die gleich oder voneinander verschieden sind, Wasserstoffatome, Gruppen $-CHR_2$ oder Gruppen -CHR-, die unter Bildung eines Rings mit 3 bis 8 Kohlenstoffatomen miteinander verbunden sind, bedeuten, worin die Substituenten R Wasserstoffatome, C_1-C_{20} Alkylreste, C_3-C_{20} Cycloalkylreste, C_2-C_{20} Alkenylreste, C_6-C_{20} Arylreste, C_7-C_{20} Alkarylreste oder C_7-C_{20} Aralkylreste sind und Si- oder Ge-Atome enthalten können;
die Substituenten R^3, R^4, R^5 und R^6, die gleich oder voneinander verschieden sind, die Definition der Substituenten R besitzen, wobei zusätzlich zwei benachbarte Substituenten R^3, R^4, R^5 und R^6 an dem gleichen Ring einen Ring mit 5 bis 8 Kohlenstoffatomen bilden können;
M für ein Übergangsmetallatom der Gruppen IVb, Vb oder VIb des Periodensystems steht;
die Substituenten X, die gleich oder voneinander verschieden sein können, Wasserstoffatome, Halogena-

tome, Gruppen-R^7, -OR^7, -SR^7, NR^7_2 oder -PR^7_2 bedeuten, worin die Substituenten R^7 wie der Substituent R definiert sind; und

(B) zumindest einer Verbindung, ausgewählt unter den organometallischen Verbindungen des Aluminiums, die zumindest ein Heteroatom, ausgewählt unter Sauerstoff, Stickstoff und Schwefel enthalten, und unter den Verbindungen, die imstande sind, ein Metallocenalkylkation zu ergeben.

2. Verfahren gemäß Anspruch 1, worin die Metallocenverbindung der Formel (I) als Reaktionsprodukt mit einer organometallischen Verbindung des Aluminiums der Formel AlR^8_3 oder $Al_2R^8_6$ vorliegt, worin die Substituenten R^8, die gleich oder voneinander verschieden sind, wie der Substituent R definiert sind oder Halogenatome bedeuten.

3. Verfahren gemäß Anspruch 1 oder 2, worin in jeder der beiden Indenyl- oder Tetrahydroindenylgruppen der Metallocenverbindungen der Formel (I) die Substituenten R^3 die gleiche Bedeutung wie der Substituent R^6 besitzen, während die Substituenten R^4 die gleiche Bedeutung wie der Substituent R^5 besitzen.

4. Verfahren gemäß Anspruch 3, worin in der Metallocenverbindung der Formel (I) die Substituenten R^3, R^4, R^5 und R^6 Wasserstoffatome sind.

5. Verfahren gemäß einem der Ansprüche 1 bis 4, worin in der Metallocenverbindung der Formel (I) das Übergangsmetall M unter Ti, Zr oder Hf ausgewählt ist.

6. Verfahren gemäß einem der Ansprüche 1 bis 5, worin in der Metallocenverbindung der Formel (I) die Substituenten X Chloratome oder Methylreste sind.

7. Verfahren gemäß einem der Ansprüche 1 bis 6, worin in der Metallocenverbindung der Formel (I) die Substituenten R^1 C_1-C_3 Alkylreste sind.

8. Verfahren gemäß Anspruch 6, worin die Substituenten R^1 Methylreste sind.

9. Verfahren gemäß einem der Ansprüche 1 bis 8, worin die organometallische Verbindung des Aluminiums, die zumindest ein Heteroatom aufweist, ein Alumoxan ist.

10. Verfahren gemäß Anspruch 9, worin das Alumoxan als Reaktionsprodukt mit einer organometallischen Verbindung des Aluminiums der Formel AlR^8_3 oder $Al_2R^8_6$ vorliegt, worin die Substituenten R^8, die gleich oder voneinander verschieden sind, wie die Substituenten R definiert sind oder Halogenatome bedeuten.

11. Verfahren gemäß Anspruch 9 oder 10, worin das Alumoxan Methylalumoxan (MAO) ist.

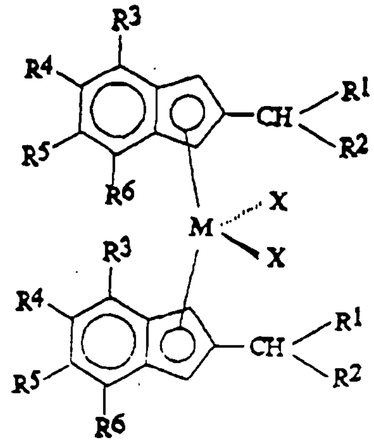
12. Verfahren gemäß einem der Ansprüche 9 bis 11, worin das Molverhältnis zwischen dem Aluminium und dem Metall der Metallocenverbindung zwischen 10:1 und 10000:1 liegt.

13. Verfahren gemäß einem der Ansprüche 1 bis 12, worin die Polymerisationsreaktion des Propylens in Gegenwart von einem oder mehreren Olefinen, ausgewählt unter Ethylen und den 4 bis 20 Kohlenstoffatomen aufweisenden α-Olefinen, durchgeführt wird.

Revendications

1. Un procédé de préparation de polymères de propylène sensiblement amorphes, présentant des enthalpies fusion de (ΔH_f) qui ne sont pas mesurables par calorimétrie différentielle à balayage, comprenant la réaction de polymérisation du propylène et, le cas échéant, d'une ou plusieurs oléfines pour obtenir un homopolymère de propylène ou un copolymère de propylène ayant jusqu'à 10 % en moles de motifs comonomères, ladite polymérisation étant effectuée en la présence d'un catalyseur comprenant le produit de la réaction entre :

(A) un dérivé métallocénique choisi parmi les dérivés de bis-indényle de formule (I):



(I)

et les dérivés correspondants de bis-4,5,6,7-tétrahydroindényle, dans lesquels :

sur chaque groupe indényle ou tétrahydroindényle, les substituants R^1 et R^2, identiques ou différents l'un de l'autre, sont des atomes d'hydrogène, des groupes $-CHR_2$, ou des groupes -CHR- unis entre eux pour former un cycle comportant de 3 à 8 atomes de carbone, où les substituants R sont des atomes d'hydrogène, des radicaux alkyle en C_1 à C_{20}, des radicaux cycloalkyles en C_3 à C_{20}, des radicaux alkényles en C_2 à C_{20}, des radicaux aryles en C_6 à C_{20}, des radicaux alkaryles en C_7 à C_{20}, des radicaux aralkyles en C_7 à C_{20} et qui peuvent contenir des atomes de Si ou Ge ;

les substituants R^3, R^4, R^5 et R^6; identiques ou différents les uns des autres, sont définis comme les substituants R, en outre, deux substituants adjacents R^3, R^4, R^5 et R^6 sur le même cycle peuvent former un cycle comprenant de 5 à 8 atomes de carbone ;

M est un atome du métal de transition des groupes IVb, Vb ou VIb du tableau périodique ;

les substituants X, identiques ou différents les uns des autres, sont des atomes d'hydrogène, des atomes d'halogène, des groupes $-R^7$, $-OR^7$, $-SR^7$, $-NR^7_2$ ou $-PR^7_2$, où les substituants R^7 ont la même définition que les substituants R ; et

(B) au moins un composé choisi parmi les dérivés organo-métalliques de l'aluminium contenant au moins un. hétéroatome choisi parmi l'oxygène, l'azote et le soufre, et entre les composés capables de donner un cation alkylmétallocène.

2. Le procédé selon la revendication 1, dans lequel le dérivé métallocénique de formule (I) est présent en tant que produit de réaction avec un dérivé organométallique de l'aluminium de formule AlR^8_3 ou $Al_2R^8_6$, où les substituants R^8, identiques ou différents, sont définis comme des substituants R ou sont des atomes d'halogène.

3. Le procédé selon la revendication 1 ou 2, dans lequel, dans chacun des deux groupes indényle ou tétrahydroindényle du dérivé métallocénique de formule (I), les substituants R^3 sont identiques au substituant R^6 tandis que les substituants R^4 sont identiques au substituant R^5.

4. Le procédé selon la revendication 3, dans lequel, dans le dérivé métallocénique de formule (I), les substituants R^3, R^4, R^5 et R^6 sont des atomes d'hydrogène.

5. Le procédé selon l'une quelconque des revendications 1 à 4, dans lequel, dans le dérivé métallocénique de formule (I), le métal de transition M est choisi parmi Ti, Zr ou Hf.

6. Le procédé selon l'une quelconque des revendications 1 à 5, dans lequel, dans le dérivé métallocénique de formule (I), les substituants X sont des atomes de chlore ou des radicaux méthyle.

7. Le procédé selon l'une quelconque des revendications 1 à 6, dans lequel, dans le dérivé métallocénique de formule (I), les substituants R^1 sont des radicaux alkyles en C_1 à C_3.

8. Le procédé selon la revendication 6, dans lequel les substituants R' sont des radicaux méthyle.

9. Le procédé selon l'une quelconque des r vendications 1 à 8, dans lequel le dérivé organométallique de l'aluminium contenant au moins un hétéroatome est un alumoxane.

10. Le procédé selon la revendication 9, dans lequel l'alumoxane est présent en tant que produit réactionnel avec un dérivé organométallique de l'aluminium de formule AlR^8_3 ou $Al_2R^8_6$, dans lequel les substituants R^8, identiques ou différents les uns des autres, sont définis comme les substituants R ou sont des atomes d'halogène.

11. Le procédé selon la revendication 9 ou 10, dans lequel l'alumoxane est le méthylalumoxane (MAO).

12. Le procédé selon l'une quelconque des revendications 9 à 11, dans lequel le rapport molaire de l'aluminium au métal du dérivé métallocénique est compris entre 10/1 et 10000/1.

13. Le procédé selon l'une quelconque des revendications 1 à 12, dans lequel on effectue la réaction de polymérisation du propylène en présence d'une ou plusieurs oléfines choisies parmi l'éthylène et les α-oléfines comportant de 4 à 20 atomes de carbone.